Well-Defined, High-Density Polymer Brushes Synthesized by Living Radical Polymerization/ A Kinetic Study on Dithioester-Mediated Living Radical Polymerization of Styrene (ORGANIC MATERIALS CHEMISTRY - Polymeric Materials)

AUTHOR(S):

FUKUDA, Takeshi; TSUJI, Yoshinobu; MURAKAMI, Syozo; OHNO, Kohji; GOTO, Atsushi; EJAZ, Muhammad; YAMAMOTO, Shinpei

Organic Materials Chemistry -Polymeric Materials-

Prof
FUKUDA, Takeshi
(D Eng)

Assoc Prof
TSUJII, Yoshinobu
(D Eng)

Instr
MURAKAMI, Syozo
(D Eng)

Instr
OHNO, Kohji
(D Eng)

Instr
GOTO, Atsushi
(D Eng)

Guest Res Assoc
EJAZ, Muhammad
(D Eng)

PD (JSPS)
YAMAMOTO, Shinpei
(D Eng)

Students

KOH, Kyoung-moo (D1) HIROSE, Yuichi (M2) YOSHIKAWA, Chiaki (M2) MARUTANI, Eizo (M1)
KWAK, Yungwan (M1) NISHIDA, Shinya (UG) SUGIYAMA, Satoshi (UG)

Scope of Research

Kinetic and mechanistic analyses are made for better understandings of the chemical and physicochemical reactions occurring in polymerization systems and for better routes to the synthesis of well-defined polymers. By various polymerization techniques, in particular, living polymerizations, new well-defined polymers or polymer assemblies are prepared, and their structure/properties relationships are precisely analyzed. Projects in progress include: (1) kinetics and mechanisms of living radical polymerization (LRP). (2) Synthesis of new polymeric materials by living polymerizations and their structure/properties studies. (3) Synthesis, properties, and applications of high density polymer brushes.

Research Activities (Year 2001)

Presentations

Kinetics of Free Radical Copolymerization, Fukuda T, IUPAC International Symposium on Free Radical Polymerization, Italy, 3-9 Jun.

Kinetics of LRP, Fukuda T, European Polymer Congress, The Netherland, 15-20 Jul.

Polymer Gels and Brushes Synthesized by LRP, Fukuda T, Gordon Research Conference on Elastomers, USA, 5-10 Aug.

LRP, Fukuda T, Summer Seminar, Soc Fiber Sci. Tech. Jpn., 5-7 Sep.

Surface Modification by LRP, Fukuda T, Controlled Polymer Synthesis, USA, 3-4 Dec.

6 Presentations, Spring Meeting, Soc. Polym. Sci, Jpn., 23-25 May. 1 Presentation, Annual Meeting, Cellulose Soc. Jpn., 12-13 Jul. 7 Presentations, Autumn Meeting, Soc. Polym. Sci, Jpn., 12-14 Sep.

Grants

Fukuda T, Structure and Properties of High-Density Polymer Brushes, Grant-in-Aid for Scientific Research. (B)(2), 1 Apr 2000 – 31 Mar 2002.

Fukuda T, Development of Living Radical Emulsion Polymerization, Grant-in-Aid for Scientific Research. (B)(2), 1 Apr 2000 – 31 Mar 2003.

Tsujii Y, Development of New Surface-Modifying Technology by LRP Method, Ind. Tech. Research Grant Program in 2000 from NEDO, 1 Nov 2000 – 31 Mar 2003.

Kaya K, Collaboratory on Electron Correlations, Grant-in-Aid for Creative Scientific Research., 1 Apr 2001, 31 Mar 2006

Topics

Well-Defined, High-Density Polymer Brushes Synthesized by Living Radical Polymerization

In recent years, surface modifications by polymers have been increasingly important for various applications ranging from biotechnology to advanced microelectronics. We were the first to succeed in applying atom transfer radical polymerization (ATRP), a variant of living radical polymerization (LRP), to the graft polymerization of methyl methacrylate, styrene, and functional monomers on a solid surface and yielding a graft layer of low-polydispersity polymer with the highest graft density reported to date. Atomic force microscopic and ellipsometric studies revealed that in such a graft layer, polymer chains are highly extended in a good solvent, nearly to their full lengths, and that the properties of these high-density polymer brushes are quite different and unpredictable from those of the "moderately dense" polymer brushes previously studied. In addition to such parameters as graft density, chain length, chain length distribution of the graft polymer, the morphology of the grafted surface was successfully controlled by the combination of surface-initiated LRP with a lithographic technique. These techniques and findings will open up a new route to "precision" modification of surfaces.

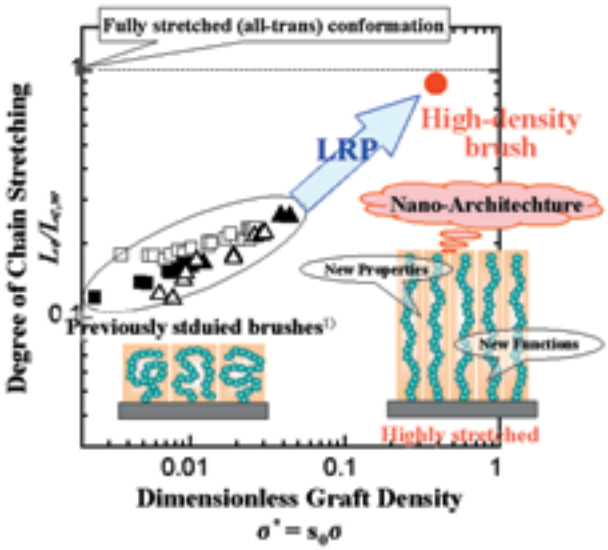

Figure 1. Relationship between graft-chain conformation and graft density in a good solvent. The vertical axis represents $L_e/L_{c,w}$, where L_e is the equilibrium thickness of the swollen brush and $L_{c,w}$ is the weight-average full length of the graft chain in the all-trans conformation. [1)] For example, see Kent et al., *J. Chem. Phys.* **1995**, *103*, 2320 & Bijsterbosch et al., *Langmuir* **1995**, *11*, 4467.

A Kinetic Study on Dithioester-Mediated Living Radical Polymerization of Styrene

In order to find a clear explanation for the rate retardation in RAFT polymerization, an on-going issue of debate, the polymerization of styrene mediated by a polystyryl dithiobenzoate was studied. Electron spin resonance spectroscopy was used to determine the concentration of the intermediate radical produced by the addition of polystyryl radical to the dithiobenzoate. The polymerization was also followed by dilatometry to estimate the concentration of the growing radical. The results showed that the fragmentation of the intermediate radical is a fast process with a relevant rate constant on the order of 10^4 s^{-1} (at 60 °C) and that the intermediate radical undergoes the cross-termination with polystyryl radical to form a 3-arm star chain, thus causing a retardation in the rate of polymerization. The rate constant of cross-termination was estimated to be similar to (somewhat smaller than) that of the termination between polystyryl radicals. The formation of the star was evidenced by a model experiment, as shown in Figure 2. The star was fairly stable at 60 °C (without decomposition for 24 h).

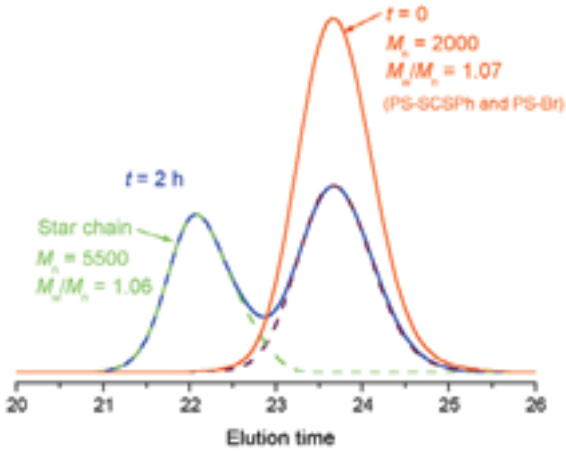

Figure 2. The GPC chromatogram for the mixture of *t*-butyl benzene, polystyryl dithiobenzoate (PS-SCSPh: M_n = 1990, M_w/M_n = 1.07), polystyryl bromide (PS-Br: M_n = 2000, M_w/M_n = 1.05), and CuBr complex heated for 2 h (60 °C). PS-Br is activated by the CuBr complex to give the polystyryl radical PS·. PS· will add to PS-SCSPh to form the intermediate radical, which subsequently will be attacked by another PS· and give a star chain. This system mimics the RAFT polymerization without propagation.